A STUDY OF CRYOSCOPIC CONSTANTS

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DAVID MUSSELMAN MUSSER

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Introduction

The purpose of this investigation was to find a solvent more suitable than camphor ($C_{10}H_{6}O$) for use in the cryoscopic molecular weight determination. The problem was extended later to include a study of the effect of constitution of a compound on its cryoscopic constant.

Historical

The possibility of using camphor as a solvent for the cryoscopic molecular weight determination was first pointed out by Jouniaux[1]. Rast demonstrated its advantages and developed the technique for micro and semi-micro cryoscopic molecular weight determinations[2]. Since it has a high freezing point lowering constant (39-40) an ordinary thermometer will give an accurate reading of the temperature difference whereas a solvent with a low constant necessitates the use of a Beckmann to insure accuracy.

(1) Bull. Soc. Chim.,11,546,722 (1912)

(2) Ber. 55,1051 (1922)

Camphor is not an ideal solvent for molecular weight determinations. Its main defects are:(1) ordinary camphor is a mixture of the dextro and laevo forms and does not have a sharp melting point which is very desirable;(2) it has a high melting point (176-177);(3) it sublimes considerably at the melting point. These objections suggested a search for a compound which possessed a high constant but none of the undesirable properties of camphor.

A survey of the literature was made in order to ascertain what constants had been recorded and to determine if possible whether any generalities might be drawn from the available data that would facilitate the search. In addition to the constants obtained from available tables and recent journals, a great many were calculated from the latent heat of fusion by an equation given by van't Hoff

$$K = \frac{RT^2M}{1000\ w\ 238.9}$$ where

K = the cryoscopic constant

R = 1.991

T = absolute temperature

M = the molecular weight

w = the latent heat of fusion in kilojoules per formula-weight

Discrepancies between constants obtained by the above

equation and those determined by experiment necessitated the checking of a few compounds, the results of which will be given in the experimenal discussion.

Experimental

In some cases the constants are not very high, therefore accurate reading of the temperature is necessary. On this basis attempts were made to use a thermocouple (copper-constantan) with a potentiometer but with the instrument available temperature could be read to only 0.1 degree Centigrade. Then the galvanometer alone was used with the thermocouple to measure variations in deflection. The cold junction was maintained with crushed ice; deflections were measured when the hot junction was inserted first into the pure solvent at the melting point and then into the mixture of the same solvent and a definite weight of solute. Here again limitations of the apparatus failed to give the desired accuracy. Attempts were made then to increase the accuracy by use of a thermopile. In all trials it was found that the limiting factor was the ability to control the rise of temperature.

It was finally decided to limit the present problem to determinations of reasonable accuracy, which would be satisfactory for a general survey; and in case of attaining our goal of a desired compound, its cryoscopic constant could then be measured more accurately

by a thermometer such as a Beckmann or by means of a thermopile. Details of the latter method have recently been published by C. Robertson and V. K. LaMer[3].

The experiments as ultimately performed were all a variation of Rast's semi-micro method. Small samples of pure material and approximately the same quantity of solvent with solute were placed in separate tubes. A glass funnel was used to prevent material depositing along the sides. The samples were melted and allowed to solidify. Both tubes were placed in the same bath and heated at a rate not exceeding one degree Centigrade rise for every six minutes. It was found that the real limiting factor was the speed with which the sample was heated. Since the melting point of the pure sample was always run simultaneously in the same bath, variations in the rate of heating were avoided.

(3) J. Phys. Chem., 35 , 1935 (1931)

As checks on the method used, determinations were run on m-dinitrobenzene, diphenyl and p-nitrailine, with the following results

Compound	K_c	Kr	K_e
m-dinitrobenzene	10.09	10.60	10.26
diphenyl	8.40	8.00	7.95
p-nitraniline	9.67	----	9.79

K_c= the constants calculated from the latent heat of fusion as recorded in the International Critical Tables, 5 ,130

K_r the experimental constant as recorded in the International Critical Tables 4 ,183

K_e = the constant determined experimentally in this investigation

All compounds examined were carefully purified.

A survey of the literature was made to check up on the constants previously determined. From a study of both the experimental constants and those calculated from the latent heat of fusion, the following generalizations were observed:

1. In a given series of compounds an increase in the length of the chain had little effect on the constant.

Table 1

Formic acid	HCOOH	2.80
Acetic acid	CH_3COOH	3.90
Butyric acid	C_3H_7COOH	4.72 #
Caprylic acid	$C_7H_{15}COOH$	4.71 #
Capric acid	$C_9H_{19}COOH$	4.74 #
Lauric acid	$C_{11}H_{23}COOH$	4.68 #
Myristic acid	$C_{13}H_{27}COOH$	4.42 *
Palmitic acid	$C_{15}H_{31}COOH$	5.47 #
Stearic acid	$C_{17}H_{35}COOH$	4.76 #
Behenic acid	$C_{21}H_{43}COOH$	4.44

This might be due to a doubling-back of the chain, which theory has been offered as an explaination in several cases.[4]

(4) J. Am. Chem. Soc., 39 ,1858,(1917)

= constants calculated from the latent heat of fusion

* = constants determined in this investigation

Those not marked were recorded in the literature

2. Substitution had a decided effect on the constant as is shown in the following tables.

Table 2

Replacement of hydrogen in the methyl group of acetic acid

Acetic acid	CH_3COOH	3.90
Monochloracetic acid	$CH_2ClCOOH$	5.21 #
Dichloracetic acid	$CHCl_2COOH$	10.50 #
Trichloracetic acid	CCl_3COOH	22.40 #
Phenylacetic acid	$C_6H_5CH_2COOH$	9.00 #
Phenylpropionic acid	$C_6H_5CH_2CH_2COOH$	8.95

Table 3

Replacement of the methyl group

Formic acid	$HCOOH$	2.84 #
Acetic acid	CH_3COOH	3.90
Benzoic acid	C_6H_5COOH	8.32
Para toluic acid	$CH_3C_6H_4COOH$	10.52 #

Table 4

Replacement of the hydroxyl group of acetic acid

Acetic acid	CH_3COOH	3.90
Acetamide	CH_3CONH_2	3.63
Acetophenone	$CH_3COC_6H_5$	5.65
Acetanilide	$CH_3CONHC_6H_5$	6.93
Para bromacetanilide	$CH_3CONHC_6H_4Br$	24.23 *

Table 5

Replacement of hydrogen in benzene

Benzene	C_6H_6	5.12
Aniline	$C_6H_5NH_2$	5.90
Nitrobenzene	$C_6H_5NO_2$	7.07
Phenol	C_6H_5OH	7.60
Benzoic acid	C_6H_5COOH	8.32
Diphenyl	$C_6H_5-C_6H_5$	8.40
Benzamide	$C_6H_5CONH_2$	9.65
Benzophenone	$C_6H_5COC_6H_5$	9.88

Table 6

Replacement of hydrogen in naphthalene and its derivatives

Naphthalene	7.00
Alpha nitronaphthalene	9.10
Beta chloronaphthalene	9.76
Beta bromonaphthalene	12.40
Beta iodonaphthalene	15.00
1,5 acetoxynaphthalene	18.50 *
1,4 dihydronaphthalene	31.60

In the above table a marked increase is observed for the halogens in the order of chloride, bromide and iodide. In Table 7 this similarity is shown in other halogen compounds.

Table 7

Hydrochloric acid	HCl	1.07
Hydrobromic acid	HBr	1.93
Hydriodic acid	HI	2.64
Para chlorotoluene	$ClC_6H_4CH_3$	5.60
Para bromotoluene	$BrC_6H_4CH_3$	8.36
Para iodotoluene	$IC_6H_4CH_3$	10.65
Chloroform	$CHCl_3$	4.79
Bromoform	$CHBr_3$	14.35
Chloral hydrate	$CCl_3CH(OH)_2$	6.54 #
Bromal hydrate	$CBr_3CH(OH)_2$	11.04
Carbon tetrachloride	CCl_4	32.30
Carbon tetrabromide	CBr_4	48.00 *

3. Not only do the different groups play an important role in influencing the constants but also the relative position of the groups within the molecule. In the aromatic series there are a great many cases which show a definite increase in the constants in the order ortho-meta-para.

Table 8

Compound	K_c	K_r	K_e
Ortho-dinitrobenzene	8.43		
Meta- dinitrobenzene	10.09	10.60	10.26
Para- dinitrobenzene	11.78		
Ortho-nitrotoluene		5.08	
Meta- nitrotoluene		6.81	
Para- nitrotoluene		7.80	
Ortho-dichlorobenzene	6.19		
Meta- dichlorobenzene	6.00		
Para- dichlorobenzene	6.96	7.45	
Ortho-dibromobenzene	10.50		
Meta- dibromobenzene	11.20		
Para- dibromobenzene	12.74	12.00	
Ortho-chloronitrobenzene		7.50	3.25
Meta-chloronitrobenzene	6.79	6.07	6.00
Para-chloronitrobenzene	11.73	10.85	
Ortho-bromonitrobenzene	10.50	9.10	
Meta- bromonitrobenzene	11.20	8.75	10.48
Para- bromonitrobenzene	12.74	11.53	

Table 8 (continued)

Compound	K_c	K_r	K_e
Ortho-bromochlorobenzene	8.79		
Meta- bromochlorobenzene	8.29		
Para- bromochlorobenzene	9.50	9.55	
Ortho-bromoiodobenzene	14.15		
Meta- bromoiodobenzene	13.44		
Para- bromoiodobenzene	15.86		
Ortho-diiodobenzene	21.57		
Meta- diiodobenzene	16.32		
Para- diiodobenzene	19.84		
Ortho-chlorophenol		7.72	
Meta- chlorophenol		8.30	
Para- chlorophenol		8.58	
Ortho-nitrophenol		7.50	
Meta- nitrophenol		7.80	
Para- nitrophenol		8.60	
Ortho-nitraniline	8.37		
Meta- nitraniline	7.91		
Para- nitraniline	9.64		

Table 8 (continued)

Compound	K_c	K_r	K_e
Ortho-dihydroxybenzene	5.49	7.13	
Meta- dihydroxybenzene	6.33	6.50	6.27
Para- dihydroxybenzene	8.38		8.43
Ortho-chlorobenzoic acid	8.46		
Meta-chlorobenzoic acid	9.87		
Para-chlorobenzoic acid	10.50		
Ortho-nitrobenzoic acid	8.85		
Meta-nitrobenzoic acid	12.20		9.08
Para-nitrobenzoic acid	9.86		
Ortho-aminobenzoic acid	9.87		
Meta-aminobenzoic acid	10.42		
Para-aminobenzoic acid	11.51		
Ortho-toluic acid	8.00		
Meta- toluic acid	10.52		
Para- toluic acid	10.23		

In studying Table 8 discrepancies were seen between the calculated and experimental values. Considerable work was undertaken to straighten out these differences and also to throw more light on ortho-meta-para relationship. In some cases variations from the ortho-meta-para increase were very slight and well within the range of experimental error. In other cases, notably the bromochlorobenzenes, bromoiodobenzenes and diiodobenzenes, the discrepancies may be due to instability or impurities since the melting point as recorded in the literature varied as much as 18 degrees. In the following compounds the calculated values differed widely from those recorded: chloronitrobenzene, bromonitrobenzene, dihydroxybenzene and nitrobenzoic acid. The cryoscopic constant was redetermined in each case with the results as recorded in the table under K_e. In all cases the correction substantiated the ortho-meta-para increase

Table 9

Constants for several polycylic ring compounds and related derivatives

Benzene	C_6H_6	5.12
Diphenylmethane	$C_6H_5CH_2C_6H_5$	6.68
Diphenyl	$C_6H_5-C_6H_5$	8.00
Diphenylether	$C_6H_5OC_6H_5$	8.00
Azobenzene	$C_6H_5NNC_6H_5$	8.30
Azoxybenzene	$C_6H_5NONC_6H_5$	8.50
Diphenylamine	$C_6H_5NHC_6H_5$	8.80
Benzophenone	$C_6H_5COC_6H_5$	9.88
Anthracene		11.65
Phenanthrene		12.00
1,4 dihydrophenanthrene		17.79 #
Bromocamphor		11.87
Camphor		40.00
Borneol		48.00 *

Table 10

Constants in the benzothiozole series

2 phenyl 6 dimethylaminobenzothiozole	7.55 *
2,2'dimethylbenzothiozole	9.75 *
2 phenyl 6 nitrobenzothiozole	10.96*
2 para-dimethylaminophenylbenzothiozole	15.63 *
2 phenylbenzothiozole	50.50 *

2 phenylbenzothiozole is a poor solvent but has the advantages of a low melting point (114°) and practically no sublimation.

Since borneol is related in structure to camphor it would be expected to show a similar high depression of the melting point. Experiments were therefore run to determine its value. By using as impurities both para-nitraniline and meta-dinitrobenzene it was found to be 48.00.(Table 9) Patterson and Blackwood recently published their results on this same compound and reported its value as 47.00[5]. But like camphor, borneol has the objectionable properties of having a high melting point (208) and subliming readily.

In studying the effect of halogens on the constants, it was seen in Table 7 that the values increased

(5) J.Chem. Soc. 5, 93 (1933)

in the order of chlorine, bromine and iodine. Since carbon tetrachloride is a good solvent and has a constant of 32.30, carbon tetrabromide should also be a good solvent and exhibit a high constant. Experiments using various organic compounds as impurities determined its value to be 48.00-49.00. This compound also sublimed considerably at the melting point and was somewhat reactive but has the advantages of being a good solvent and having a low melting point (94).

Conclusions

1. A new variation of Rast's method was outlined for the determination of the cryoscopic constants.

2. From a survey of the constants it was seen that (a)increase in the molecular weight does not necessarily increase the constant (b)substitution and the relative position of the groups within the molecule affect the constant (c) isomers of the disubstitution class of aromatic compounds show increase in the constants in the order ortho-meta-para.

Three organic solvents--carbon tetrabromide, borneol and 2 phenylbenzothiozole-- were found to have constants as high or higher than camphor but in all cases some undesirable properties offset their qualifications as an ideal solvent.